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LOW MOLECULAR WEIGHT CARBOXYLIC ACIDS IN THE SEA  
PHOTOOXIDATIVE PRODUCTIO. (U) ROSENSTIEL SCHOOL OF  
MARINE AND ATMOSPHERIC SCIENCE MIAMI FL. K HOPPER

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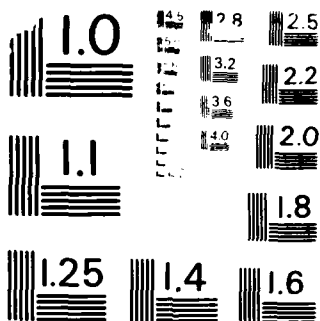
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MICROCOPY RESOLUTION TEST CHART  
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# FINAL REPORT

LOW MOLECULAR WEIGHT CARBOXYLIC ACIDS IN THE SEA:  
PHOTOOXIDATIVE PRODUCTION AND BIOLOGICAL CYCLING

ONR Contract no.: N00014-85-C-0020

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## Long-Range Scientific Objectives

A large fraction of dissolved organic matter (DOM) in seawater is composed of biologically refractory substances. The formation and destruction pathways of this organic matter are still unknown. One potentially important removal pathway that has not been quantified is sunlight-induced (photochemical) break down of DOM in the sea surface. Important breakdown products should include biologically utilizable compounds, especially low molecular weight (LMW) carboxylic acids, formate and acetate, and  $\alpha$ -keto acids glyoxylate and pyruvate. Therefore, we propose to examine organic acid photo-production in seawater as a tool to evaluate the importance of photo-fragmentation of biologically refractory organic matter in the sea. Laboratory studies will be integrated with a sea-going program, SOLARS, to establish a broad data base for the spatial and temporal distribution of organic acids in coastal and oceanic waters. With this data base, and associated biological turnover and photochemical production measurements, it will be possible to determine the importance of photochemical production of these compounds relative to their biological turnover and geochemical cycling in the sea.

DECLASSIFICATION STATEMENT A

Approved for public release  
Distribution Unlimited

## FINAL REPORT

Below is a summary of accomplishments and areas of progress during 1 October, 1986 - 30 September, 1987 on contract # N00014-85-C-0020. Various supportive documents are appended.

1. We were organizers and major participants on three oceanographic cruises as part of the SOLARS program (a description of SOLARS is appended). SOLARS 11, 3-12 Dec., 1986 (K. Mopper, chief scientist) and SOLARS 13, 27 May - 2 June, 1987 (K. Mopper, chief scientist) were conducted on the R/V Iselin (cruise # CI-8612 and CI-8703) in the central Sargasso Sea. SOLARS 14 (R. Zika, chief scientist) was also conducted on the R/V Iselin (CI8704), 27 July - 18 August, 1987, in the Gulf of Maine.

2. The major factors affecting the distribution of alpha keto acids are photochemical production, biological turnover and physical mixing. In certain coastal environments, the interaction between photochemical production and biological turnover results in strong diurnal variations of these compounds in surface waters, which is in agreement with our laboratory studies. These variations were not seen in the central Sargasso Sea probably as a result of lower photochemical production rates and biological patchiness. Below the photic zone the distributions of alpha keto acids appear to be controlled by biological processes and often show strong correlations with distributions of dissolved free amino acids.

3. Laboratory and shipboard experiments were performed to determine the degree of coupling between photochemical production of alpha keto acids (glyoxylate and pyruvate), and their biological uptake. Surprisingly, a very tight coupling was found for both open ocean and coastal surface waters. Our results demonstrate that photooxidation of biologically recalcitrant organic matter can form products that are important biological substrates. This finding has important implications regarding the cycling of DOM in the ocean. These exciting results will be presented at the upcoming AGU-ASLO meeting.

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4. Regarding carbon cycling, on recent cruises we determined that DOM in deep seawater (>1000 m) is photochemically more reactive and labile than DOM in surface waters by about a factor of four. Using the photochemical production rate of LMW carbon compounds when deep seawater samples are exposed to sunlight, we estimated the impact of photooxidation on the geochemical turnover of organic carbon in the ocean. These estimates suggest that this process is significant, although more photochemical and photophysical measurements are needed before it can be properly evaluated. These preliminary results are also being presented at the AGU-ASLO meeting.

5. We are systematically testing a variety of techniques for extracting humic substances from seawater. We are comparing various solid phase column procedures with ultrafiltration procedures. The optimal technique(s) will be used to concentrate sufficient marine humic material so that joint photochemical experiments with Rod Zika can be carried out.

6. We have begun to determine action spectra (wavelength dependence of the apparent quantum yield) for the photoproduction of alpha keto acids in seawater. This work is being done cooperatively with Rod Zika.

7. Using  $^{14}\text{C}$ -labelled compounds we conducted experiments to evaluate the photochemical incorporation rate of alpha keto acids (glyoxylate) into seawater DOM. Results to date indicate that this rate is orders of magnitude lower than photochemical production rates of these compounds from DOM.

8. Also using  $^{14}\text{C}$ -labelled compounds, we studied the photochemical decomposition of alpha keto acids in seawater samples from diverse coastal and open ocean sites. Decarboxylation was the major decomposition pathway for both glyoxylate and pyruvate in all samples and accounted for an underestimation of photoproduction rates by about 4 %. Decarboxylation appears to result from secondary photochemical processes (eg, photosensitized reactions) in seawater. Decarboxylation is readily detected at sub - low nM levels and represents one of the few clearly defined and easily studied photoreactions in seawater.

9. Two HPLC methods for the determination of sub nM levels formate and acetate in seawater have been tested and are near completion.

## PUBLICATIONS AND ABSTRACTS

### Publications:

(1986) Mopper, K. Organic chemical dynamics of the mixed layer: Measurement of dissolved hydrophilic organics at sea. In: Dynamic Processes in the Chemistry of the Upper Ocean (J.D. Burton, P.G. Brewer and R. Chesselet, Eds.). pp. 137-157, Plenum.

(1986) Kieber, D.J. and K. Mopper. Trace determination of alpha-keto acids in natural waters. Anal. Chim. Acta, 18: 129-140.

(1987) Kieber, D.J. and K. Mopper. Photochemical formation of glyoxylic and pyruvic acids in seawater. Mar. Chem. 21: 135-149.

(1987) Mopper, K. and R.G. Zika. Free amino acids in marine rains: Evidence for oxidation and potential role in nitrogen cycling. Nature, 325: 246-249.

(1987) Mopper, K., Zika, R. and Fischer, A. Photochemistry and photophysics of marine humic substances. In: Humic Substances: IV (P. MacCarthy, E.T. Gjessing, R.F.C. Mantoura and P. Sequi, eds.), Wiley, Accepted.

(1987) Kieber, D.J., Vaughan, G. and Mopper, K. Enzymatic determination of formic acid in natural waters. Anal. Chem., submitted.

(1987) Kieber, D.J., McDaniel, J.A. and Mopper, K. Photochemical and biological regulation of glyoxylic and pyruvic acid concentrations in the upper ocean. In preparation.

Kieber, D.J., Mopper K. and McDaniel, J.A. Photochemical decarboxylation of pyruvic and glyoxylic acids in seawater. In preparation.

(1987) Kieber, D.J. and Mopper, K. Distribution of alpha keto acids in the sea. In preparation.

(1987) Kieber, D.J. and Mopper, K. Evaluation of precursors and pathways in the photochemical formation of alpha keto acids in seawater. In preparation.

**Published Abstracts** (several oral presentations will be given at the AGU-ASLO Ocean Sciences Meeting, Jan. 1988):

(1986) Mopper, K. Potential impact of photooxidative cleavage of humic substances on the cycling of carbon in the sea. Abstracts of Papers of the Am. Chem. Soc. 191, April, 1986.

(1986) Mopper, K. and D.J. Kieber. Redox sensitive organic compounds in the chemocline of the Cariaco Trench. Extended Abstract. In: The Chemistry and Physical Oceanography of the Black Sea, (D. Dyrssen, Ed.), Report on the Chemistry of Seawater. XXXIII. University of Göteborg, Sweden.

(1986) Mopper, K. and D.J. Kieber. Cariaco Trench 1986: Redox sensitive organic compounds in the chemocline of the Cariaco Trench. Trans. Am. Geophys. Un. 67: 1067.

(1987) Kieber, D.J., G. Vaughan and K. Mopper. Enzymatic determination of formic acid in natural waters. Abstracts of Papers of the Am. Chem. Soc. 194, Sept. 1987.

(1987) Mopper, K., Sikorski, R.J., Kieber, D.J. and McDaniel, J.A. Photochemical incorporation and fragmentation of DOM in relation to oceanic carbon cycling. Trans. Am. Geophys. Un. 68, in press.

(1987) Kieber, D.J., McDaniel, J.A. and Mopper, K. Photochemical and biological regulation of glyoxylic and pyruvic acid concentrations in the upper ocean. Trans. Am. Geophys. Un. 68, in press.

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